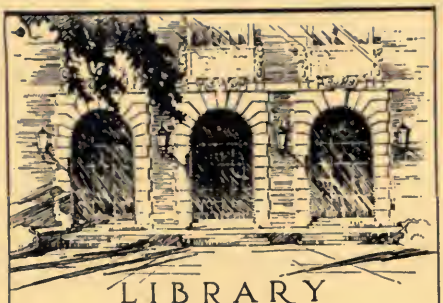

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The Migration of Iron and Manganese in Colloidal Systems

By

Eric Winters

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The Migration of Iron and Manganese In Colloidal Systems[a]

By Eric Winters, formerly Associate in Soil Physics and Soil Survey

BECAUSE the translocation of secondary products and their subsequent redeposition is perhaps the most important cause of horizon differentiation in soils, any knowledge concerning the movement of the products of weathering is likely to be helpful in tracing the course of soil genesis. In a report[55*] in 1938 by the present author, the general occurrence of ferromanganiferous[b] concretions thruout the profiles of certain podsolic soils presenting a very wide range in reaction, texture, organic-matter content, drainage, and stage of development was described, tho the genesis of these accumulations—particularly the manner in which the iron and manganese moved to the centers of concretion formation—was not explained. In the present bulletin an approach is made to this problem of translocation by attempting to define the conditions and manner of iron and manganese migration in certain colloidal systems whose properties are similar to those of soils. The question of aggregation is not discussed, tho it is recognized that a thoro treatment of the genesis of any secondary accumulation should consider the mode of precipitation and consolidation, as well as the migration to the center of aggregation. Obviously, the problem of migration must first be elucidated before the question of precipitation can be adequately approached.

Many phases of the general problem of transport of secondary materials in soils are not well understood in spite of a voluminous literature on the subject. The translocation of manganese, for example, has seldom been mentioned; and on the problems of iron migration little has been added to the discussions made in the rather early treatises of Frosterus[17*] and more particularly those of Aarnio,[1*] despite the fact that those fell short of adequate explanations. Frosterus[17*] observed the occurrence of "Rostroehrchen Konkretionen"

*These numbers refer to literature citations on pages 141 to 143.

[a]Based on a thesis submitted by Eric Winters to the Graduate School of the University of Illinois, August, 1938, in partial fulfillment of the requirements for the degree of doctor of philosophy in agronomy.

[b]The concretions were called "ferromanganiferous" because of their high content of iron and manganese and low content of organic matter, as compared with the soil matrix.

and suggested that they were formed from iron that percolated down root channels in the ionic form, as a complex humate, as a sol, or perhaps in all three forms. He also postulated a mechanism of aggregation. Aarnio,[1*] besides completely reviewing the available literature, worked out in some detail the conditions under which iron sols were stable and mobile, as well as those conditions which caused their flocculation and immobilization. He also considered the formation of complex humates and the reduction of iron to give ferrous ions in the soil.

Inasmuch as the general conclusions reached by these investigators have been altered but little by subsequent work, no review of the later literature is given here. It seems likely that the failure to further clarify the mechanism of transport has largely been due to the complexity of the soil system. For this reason, the experimental work in the present investigation was conducted not with a soil system itself but with simpler systems having comparable properties.

MATERIALS AND METHODS

The Soil as a Gel System.—Soils under natural field conditions are three-phase systems that have many properties in common with gels. Freundlich[13*] defined gels broadly as "colloidally disperse structures consisting of a solid and a liquid phase . . . . and having shape and cohesion" (p. 658). True gels are thus two-phase systems, both phases of which are continuous. Certain important properties attach to gels because of their polyphasic nature. Svedberg[50*] emphasized the absence of convection currents, which means that transport must be entirely by diffusion (p. 245). The slowness of transport by diffusion permits localization of many reactions. The familiar Liesegang phenomenon is cited by Svedberg as the classic example of such localization of reactions.

In another paper Freundlich[14*] pointed out that pastes, which like soils contain numerous large particles in addition to those of colloidal size, are systems similar to gels in most of their properties. Unlike pastes, however, soils usually have pores that are filled with air. Soil systems thus consist of three phases—solid, liquid, and gaseous. Frequently the pores may be so interconnected as to constitute channels that permit transport by convection in the soil during wet periods. This situation is particularly prominent in sandy soils, and when the texture

is very coarse the analogy to a gel system may well be abandoned. In soils of silt and clay-loam texture, however, convection is restricted largely to root channels, animal burrows, and the major structure seams, except in the surface horizon which is disturbed by cultivation. It is to be expected therefore that in heavy-textured soils such processes as diffusion will closely parallel those in the simple gels.

The Gels Used.—On the basis of certain recent investigations on the nature of soil colloids, a simple system prepared from bentonite was chosen as a substitute for soil. Hofmann, Endel, and Wilm[22*] have shown that montmorillonite, the chief constituent of bentonite, has a crystal structure very similar to that of the colloidal clays, which constitute the "active" gel surface of the soil systems in podsolic regions. The montmorillonite of bentonite can be readily purified by electrodialysis, is white in color, and free of organic matter. Gel systems prepared from bentonite thus have several distinct advantages over natural soil systems for the study of transport: they are free of the many unknown compounds that obscure the interpretation of results in soils; their color permits observation of the diffusing particles; the absence of pores eliminates the possibility of confusing diffusion with convection.

Gels of agar, gelatin, and silica were also used in order to broaden the scope of the observations.

Preparation of Gels.—The gels were prepared in the following manner:

Bentonite gels. Material smaller than one micron was separated from the natural bentonite and electrodialyzed several months to remove all diffusible ions. The resulting sol, whose pH was 2.8 and concentration about 4 percent, was poured into a tube and centrifuged. The bentonite sedimented somewhat and the supernatant liquid was then decanted, leaving a thixotropic gel whose concentration averaged about 5 percent.

Agar and gelatin gels. The commercial dry materials were dissolved in the usual manner by heating with water and were poured while hot into tubes to solidify.

Silica gels. Sodium silicate was neutralized with HCl and the precipitate electrodialyzed two weeks. The resulting sol was centrifuged to a gel in the same manner as the bentonite.

Tubes of 10 ml. capacity were used thruout to keep at a minimum the quantity of materials needed for the gel systems. All pH measurements were made with a Coleman glass electrode.

Further details of procedure are discussed in connection with the particular experiments to which they apply.

STABILITY AND DIFFUSION OF SOLS[a]

The behavior of colloidal suspensions of insoluble materials was the object of investigation in the first part of the study. As has already been mentioned, transport in gel systems must be by diffusion. The probability of transport of a given sol system by convection can, however, be inferred from its stability. Some attention was therefore given to the flocculation behavior of sol systems (i.e., dilute colloidal suspensions).

To study the diffusion of a sol, about 1 ml. of the sol was pipetted on top of the prepared gel in a culture tube so that the layer of sol was about 1 cm. deep. Observations were made at convenient intervals, diffusion being detected by the advance of the colored or opaque sol particles into the colorless or white gel. Sols other than those of iron and manganese were also used, in the expectation that these additional systems might yield data that would help in interpreting the behavior of the iron and manganese sols.

Each sol system is discussed separately as to preparation, properties, and diffusibility. Uncertainty exists as to the composition of many sol micelles, as has been clearly pointed out by Mellor[36*] in regard to sols of ferric hydroxid. The sols are therefore designated by convenient symbols, such as $Fe(OH)_3$, without any implication thereby as to micelle composition. Whether a sol was charged positively or negatively was determined by electrophoresis in a Burton tube, as outlined by Hatschek.[21*]

Single Sols

$Fe(OH)_3$ Sols.—Three $Fe(OH)_3$ sols were prepared, all by the same general method, namely, by heating $FeCl_3$ with $(NH_4)_2CO_3$. The resulting sols were dialyzed one week, at the end of which time only a faint test for chlorids was obtained. Sol 1 was a year old, yellow, and contained .43 percent Fe_2O_3 by weight. Sol 2 was freshly prepared, yellow, and more dilute (concentration .10 percent). A solution of N/20 $FeCl_3$ was used for Sol 3; the temperature was kept lower than for the other two sols (about 80° C.); and an orange-red sol was obtained having a concentration of .27 percent. From the color it was assumed that the particles of Sol 3 were smaller than those of

[a]Many of these experiments on the stability and diffusion of sols were performed in the soils laboratory at the University of Missouri, where the author spent a three-month leave of absence in 1936. The collaboration of the members of the Soils Department there, particularly of Hans Jenny, Assistant Professor of Soils, and the kindness of all concerned in making the laboratory facilities available for these experiments, is hereby gratefully acknowledged.

Sols 1 and 2. All three sols were positive, since they migrated to the cathode in a Burton tube.

Tho numerous trials were made, no diffusion could be detected with any of the $Fe(OH)_3$ sols in agar, bentonite, gelatin, or SiO_2 gels. Partial to complete flocculation occurred in less than a day except on the SiO_2 gel. Sol 3 was stable on this medium for two days, after which time flocculation gradually took place.

Since the $Fe(OH)_3$ sols are positive while the bentonite is negative, the flocculation could be explained as mutual coagulation. Gelatin is amphoteric and becomes positively charged below its isoelectric point, which, according to Loeb,[34*] is 4.8. The Fe sols (Fe will be written for $Fe(OH)_3$ hereafter) still flocculated when in contact with the gelatin whose pH had been adjusted with HCl to 4.2. Fresh gelatin brought to pH 3.8 also induced flocculation of the Fe sols. Thus it seems that Fe sols are not stable enough to permit diffusion in most gel systems, tho movement thru large pores by convection, as reported by Jenny and Smith[27*] is possible. However, Demolon and Batisse[10*] observed that Fe sols flocculated on the surface of soil columns whose pores were presumably small, and were then unable to migrate.

The ease of flocculation of the Fe sols is related to their hydrophobic nature, stability being almost entirely due to the zeta potential, as pointed out by Kruyt[30*] for hydrophobic systems in general. Ionic exchange incident to contact with the gel medium would readily lower the zeta potential below the critical value and induce flocculation. The instability of the Fe sols was further shown by their inability to withstand electrodialysis for more than a few hours without irreversible flocculation. It was for this reason that they were freed of ions by ordinary dialysis.

Powis[46*] obtained negative Fe sols by adding $FeCl_3$ to an excess of NaOH. The sols thus obtained, however, flocculated on dialysis. The charge of positive Fe sols can be reversed with polyvalent anions such as arsenious acid, as described by Sen, Ganguli, and Dhar.[47*] Other methods of obtaining negative Fe sols are essentially variations of these two. Since Fe sols of the type thus produced are unlikely to occur in any ordinary soil system, they were not studied in this investigation. The "negative" Fe sols reported by Barbier[4*] are nothing more than "protected" sols, which will be discussed later (page 113).

MnO_2 Sol.—The method of Ghosh and Dhar,[18*] slightly modified, was used to prepare this sol. Briefly, that method consists of treating $KMnO_4$ with H_2O_2 and dialyzing the precipitate for eight days. The resulting sol had a concentration of .03 percent, and was negative.

The behavior of the MnO_2 sol on bentonite and gelatin was similar to that of the Fe sols. Flocculation occurred within one or two days, with no evidence of diffusion. On the SiO_2 and agar gels, the MnO_2 sol was stable indefinitely, and diffused to a depth of 1 to 2 mm. in 1-percent agar in the course of three months. No diffusion was observed in the SiO_2 gel, however, perhaps because of its greater concentration and correspondingly smaller capillary-pore size.

The extremely slow rate of diffusion indicates that effective migration of manganese in the sol form would be restricted to convection thru pores, as with the Fe sols.

Organic-Matter (Humus) Sols.—Two organic-matter sols, hereafter abbreviated as O.M. sols, were used. O.M. Sol 1, whose pH was 8.0 and concentration .13 percent, was a humus extract from peat. It was already available, having been prepared at the University of Missouri before these experiments were begun. O.M. Sol 2 was a water extract of partially decomposed leaves from deciduous hardwoods. The leaves were shaken overnight and the extract filtered thru a coarse paper giving a sol of pH 6.0 and concentration .10 percent. Both sols were negative.

The dark-colored particles of both O.M. sols diffused into all the gel systems used. At the greater depths of penetration, the color in the gel was yellowish or brown, whereas nearer the interface of gel and sol a darker color obtained. The possibility that the yellowish particles were smaller was verified in the following manner. Some of each O.M. sol was placed in a collodion bag and suspended in water. Sol 2 showed diffusion into the external liquid within a day, and Sol 1 in three days. The diffusate was a golden yellow in each case, in contrast to the dark brown color of the sol within the bag. Thus not only do O.M. sols contain very small particles, but these particles are light colored and thus account for the color differences in the gels resulting from diffusion of the O.M. sols in them.

One might be inclined to question the colloidal character of particles small enough to diffuse thru collodion. Later experiments, however, showed that these O.M. sols were completely flocculated by Fe sols when added in proper quantity. Also electrolytes caused flocculation in the expected manner. Therefore disperse systems containing organic matter, as well as those containing proteins, may well be classed with the sols.

The rate of diffusion of the O.M. sols was not easy to judge accurately because the advancing boundary was indistinct, owing to the difference in speed of the various-sized particles. In 1-percent agar the

boundary moved down about 3 to 4 mm. a day, while in bentonite and 5-percent gelatin the rate was somewhat slower, 2 to 3 mm. a day.

Particles composing most organic sols are known to be hydrophyllic in nature. Consequently the O.M. sols should be more stable than those of the hydrophobic type, since in addition to the zeta potential the added factor of hydration is acting to prevent coagulation.[30*] How potent a stabilizing factor the polarized water hull around the particles is, will be apparent from the data on flocculation values which follow on page 110. The combination of great stability and small micelle size then accounts for the ready diffusion of the O.M. sols, in contrast to that of the iron and manganese sols.

Gold Sol.—Colloidal gold was prepared by the reduction of $AuCl_3$ as described by Holmes.[23*] The resulting sol was cherry red and negative. It was quite stable on 1-percent agar, but diffusion was very slow, two weeks being required to move down 1 mm. In three months it had diffused a distance of 6 mm. without any indication of flocculation. The maximum diffusion of gold in bentonite was 1 mm. On bentonite flocculation was noticeable at the end of a week, and in three weeks it was complete.

Since the gold sol, like the Fe sols, was hydrophobic, the fact that its stability was greater than that of the Fe sols may be attributed to some protective action exerted by the tannin used in its preparation. Protective action will be discussed at some length below (pages 110 to 113) as being important in promoting the stability and migration of other hydrophobic sols.

Clay Sol.—Sodium hydroxid was added to electrodialyzed Putnam clay in sufficient quantity to saturate the exchange complex. The resulting sol was yellowish brown, negative, and had a total clay content of .5 percent. It was stable on 1-percent agar, but no evidence of diffusion could be seen within a week. Two weeks were required for its particles to penetrate to a depth of 1 mm. Since clays are heterodisperse, the advancing boundary was indefinite, as were the boundaries also with the heterodisperse O.M. sols. Measurements for longer periods of diffusion therefore were not exact. There was evidence, however, of diffusion to a depth of 6 or 7 mm. after a period of ten weeks.

In contact with bentonite gels, the Na-Putnam sol gradually flocculated, probably because of ionic exchange (H for Na) and consequent lowering of the zeta potential below the critical value.[26*] In two weeks flocculation was complete. Fresh sol added to the same gel remained stable for another two weeks, but no diffusion into the bentonite

occurred. The greater flocculating activity of the bentonite than of the agar, evident thruout these experiments, can be partly explained not only by the greater concentration of the bentonite, but also by its higher exchange capacity.

Mixed Sols

Protective Action.—When the addition of one sol to another increases the stability of the latter, it is said to be protected by the first. In general, hydrophyllic sols, such as those of organic matter, exert a protective action on hydrophobic sols when added in proper amount.[13*]

Protection probably results from the coating of the hydrophobic sol with particles of the protecting one. This conclusion is corroborated by the data of Abramson,[3*] who added protein solutions to a suspension of quartz particles and observed that the quartz then behaved as did the protein, both in an electric field and toward flocculation by electrolytes. Aarnio[1*] noted that within a certain range of concentration, organic matter flocculated Fe sols, but beyond this range no flocculation occurred. Therefore the first step in a study of the diffusion of protected Fe sols is to determine the appropriate ratio in which to add the protective agent.

Flocculation Values of Mixed O.M. and Fe Sols.—One way to express quantitatively the stability of a colloidal system is in terms of the concentration of a given electrolyte required to produce flocculation. Thus a sol requiring a 1-percent concentration of NaCl to flocculate it is less stable than one which is flocculated only by 5-percent NaCl. Stability of the above two systems may then be stated in terms of "relative flocculation values" (abbreviated as F.V.), which, in this case, would be 1 and 5 respectively.

The F.V.'s of the O.M. and Fe sols alone and mixed in various proportions were determined (Fig. 1) essentially as outlined by Michaelis,[37*] using KCl as the electrolyte. The Fe sol used had an F.V. of 1.5, corresponding to the broken line across the graph. O.M. Sol 1 had an F.V. of approximately 20 and O.M. Sol 2 about 30, a very great stability in comparison with that of the Fe sol. An F.V. of 0, where the curves touch the abscissa, indicates mutual coagulation and corresponds to the range of precipitation reported by Aarnio[1*] for similar systems. Values between 0 and 1.5 represent various degrees of sensitization or decreased stability.[30*] It will be noted that sensitization resulted until the proportion of organic matter by weight reached 40 percent in O.M. Sol 2 and 55 percent in O.M. Sol 1. As the pro-

portion of organic matter was further increased, the F.V. rose rapidly, indicating the greater stability of the mixed sols with a high O.M. content.

In discussions of sol stabilization the statement frequently appears that very small amounts of organic matter will stabilize Fe sols. It is true that the absolute concentration in grams per liter is small, but the ratio of Fe_2O_3 to organic matter is seldom wide when protection results. Moore and Maynard[39*] considered in some detail the protec-

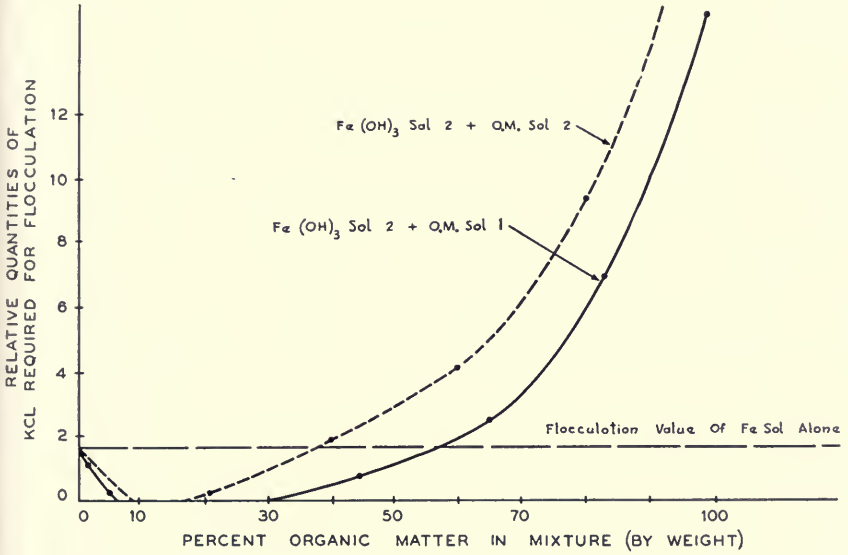


FIG. 1.—FLOCCULATION VALUES OF O.M. AND FE $(OH)_3$ SOLS MIXED IN VARIOUS PROPORTIONS

tive action of organic matter on Fe sols. They found that the Fe content in the sol form in several streams and lakes varied directly with the amount of organic matter present. The ratio of organic matter to Fe_2O_3 approximated 3 to 1, tho in some cases it was as low as 2 to 1 and even 1 to 1. In laboratory experiments with artificial sols, they obtained stable mixtures when the ratio was 1 to 1 and 1 to 2. Since they did not give the relative flocculation values, it is not possible to compare the stability of the mixtures with that of the original sols. Aarnio[2*] reported that the range of mutual flocculation of O.M. and Fe sols may extend to ratios of 3 to 1 in extreme cases. Thus the conclusion seems justified that for effective protection under most

conditions, the quantity of organic matter present must be at least approximately equal to the quantity of Fe_2O_3.

Diffusion of Fe Sols Protected With Organic Matter.—In order to double the stability of Fe Sol 2 it is necessary to add O.M. Sol 2 in such quantity that approximately 50 percent of the total solids present by weight in the mixture shall be organic (Fig. 1). When O.M. Sol 1 is used, about 70 percent of the mixture (by weight) must be organic in order to double the stability. Two mixed sols containing these respective amounts of organic matter and Fe_2O_3 were placed on bentonite and on agar.

On the bentonite gel, both mixed sols showed slight flocculation within two days, and in ten days considerable flocculation had occurred. No diffusion of the reddish Fe particles could be seen. Apparently larger proportions of organic matter are necessary to stabilize Fe sols in the presence of bentonite. However, the contrast in stability to that of the unprotected Fe sols, which flocculated over night on bentonite, is marked.

Both sol mixtures on 1-percent agar showed evidence in about a week that the reddish-brown Fe particles were diffusing. In a month the Fe particles appeared to have reached a depth of 5 mm. Some O.M. particles had diffused far beyond this distance, but it was not difficult to distinguish the Fe particles from them. After three months the mixed sols on agar had shown no sign of flocculation. The Fe sol protected with O.M. Sol 1 had diffused approximately 15 mm., while the one protected with O.M. Sol 2 had diffused about 12 mm. Apparently Fe particles are small enough to diffuse slowly in dilute gels if they can be adequately stabilized. This conclusion is corroborated by the data of Nickols, Kraemer, and Bailey[40*] in regard to the particle size of Fe sols prepared in a similar manner.

Other Protected Fe Sols.—Udluft[53*] reported that MnO_2 sols are more stable, particularly in the presence of carbonates, than Fe sols, and suggested that Mn sols may protect Fe sols in some cases. He found that the two sols mutually flocculated within a certain range of concentrations, but were stable beyond this range. The Fe sol could thus acquire the properties of the Mn sol.

In the experiments reported here the previously prepared Mn sol and Fe Sol 3 were mixed in various proportions to determine the ratio for stability. Partial to complete flocculation occurred until the ratio of MnO_2 to Fe_2O_3 in the resultant mixture was 4 to 1 by weight. Since the amount of Mn in soils is very low in comparison to the amount of Fe, it is doubtful if Mn would ever be an important protective agent

for the translocation of Fe. Furthermore, the behavior of the stable Mn-Fe mixed sol should approximate that of the Mn sol alone. In view of these facts, no diffusion experiments were attempted.

Moore and Maynard[39*] found some protective action exerted by colloidal silica on Fe sols. The "negative" Fe sols of Barbier[4*] already mentioned belong to this class. Since SiO_2 does not accumulate in the ferromanganiferous concretions, iron-silica sol mixtures were not studied.

General Discussion of Sol Stability and Diffusion

The data so far presented on the diffusion behavior of the various sols are summarized in Table 1. Three situations are evident: (1) flocculation and no diffusion; (2) stability but no diffusion; and (3) stability and diffusion. The rate of diffusion, except in the instance of the O.M. sol, was very slow, a few millimeters per month. Micelles only slightly larger than big molecules were shown to be present in the O.M. sols.

On theoretic grounds a very slow rate of diffusion is to be expected for most colloidal particles. The relation between "specific diffusion rate," D, according to Thomas,[51*] and the radius, r, of the moving particle is given by Einstein's equation:

$$D = \frac{RT}{N6\pi nr}$$

This equation assumes spherical uncharged particles of radius r in a liquid of viscosity n; R is the gas constant; T, the absolute temperature; and N, Avogardo's number. Freundlich[13*] quotes data on the diffusion of gamboge, which can be well expressed by the equation. In Fig. 2 are shown the values of D corresponding to radii between 1 and 40 Å. This range represents the range from ions thru molecules to the smaller colloid micelles. Ions and other charged particles will move faster than the equation indicates, but this correction is not important here. The significant fact is that D becomes very small near the upper limit of molecular dimensions (10 Å); and for the smaller colloidal particles with radii of only 30 to 40 Å the "specific diffusion rate" approaches a negligible value. True diffusion of sols would thus be restricted to those whose particles fall in the lower range of colloidal dimensions, and even then the rate would be very slow compared to that of rather large molecules.

For diffusion in gel systems interaction must not occur with the gel material and the diffusing particle must be smaller than the in-

TABLE 1.—SUMMARY OF DATA ON DIFFUSION AND STABILITY OF SOLS

Sol system	Charge	Concentration	Behavior of sol on—							
			1-percent agar gel		5-percent bentonite gel		5-percent gelatin gel		Silica gel	
			Stability	Diffusion	Stability	Diffusion	Stability	Diffusion	Stability	Diffusion
Fe(OH)₃										
Sol 1	Positive	.43%	Flocculated	None	Flocculated	None	Flocculated	None	.....	.....
Sol 2	Positive	.10%	Flocculated	None	Flocculated	None	Flocculated	None	.....	.....
Sol 3	Positive	.27%	Flocculated	None	Flocculated	None	Flocculated	None	Flocculated slowly	None
Organic matter										
Sol 1	Negative	.13%	Stable	3-4 mm./day	Stable	2-3 mm./day	Stable	2-3 mm./day	.....	.....
Sol 2	Negative	.10%	Stable	3-4 mm./day	Stable	2-3 mm./day	Stable	2-3 mm./day	.....	.....
Gold	Negative	(a)	Stable	2 mm./month	Flocculated slowly	None	.....	.....	.....	.....
Na-Putnam	Negative	.5%	Stable	2 mm./month	Flocculated slowly	None	.....	.....	.....	.....
$Fe(OH)_3$ Sol 2 / O.M. Sol 1	Negative	30:70 parts	Stable	5 mm./month	Flocculated slowly	None	.....	.....	.....	.....
$Fe(OH)_3$ Sol 2 / O.M. Sol 2	Negative	50:50 parts	Stable	4 mm./month	Flocculated slowly	None	.....	.....	.....	.....
MnO_2	Negative	.03%	Stable	1-2 mm./3 mo.	Flocculated	None	.....	.....	Stable	None

[a] Not determined.

terstices of the gel structure. In dilute gels many electrolytes, because of the small size of their ions, diffuse as readily as in water, but when the concentration of the gel is greater, diffusion is retarded somewhat.[51*] Because the micelles of most sols are large in comparison to molecules and ions, the diffusion of sols would be much more seriously

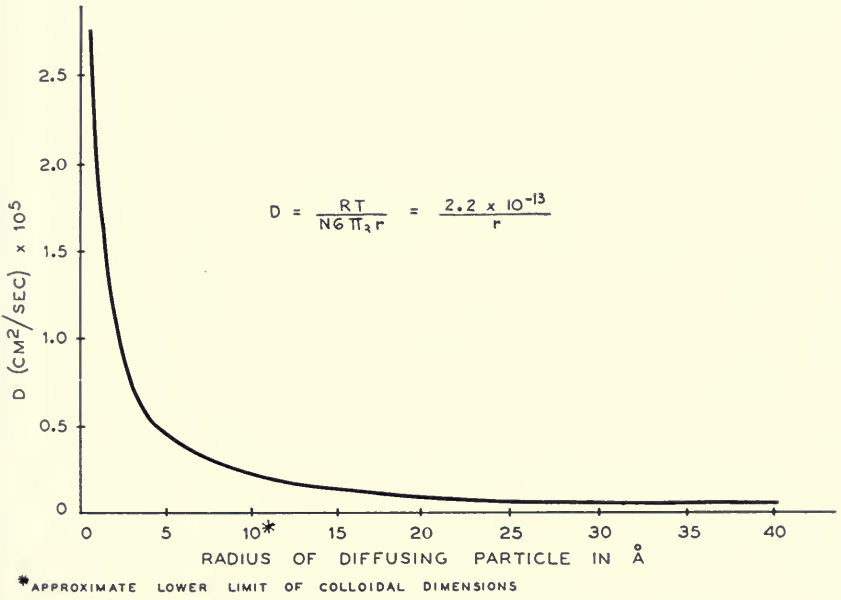


FIG. 2.—RELATION OF SPECIFIC DIFFUSION RATE (D) TO THE RADIUS OF THE DIFFUSING PARTICLE

impeded by the gel structure. The effect is well illustrated by Freundlich's data[13*] on the diffusion of dyes in 5-percent gelatin, the rates being only ⅓ to $\frac{1}{10}$ of those observed in water.

On the basis of these considerations, the three situations with respect to the diffusion behavior of sols noted above can be readily explained:

1. Flocculation, from whatever cause, greatly increases the size of the micelles. The resulting particles are too large either to penetrate the gel capillaries or to diffuse at an appreciable rate in a free liquid. The diffusion of a sol that is stable naturally or because of the addition of such a protective agent as O.M. sols, would depend on the relation of micelle size to capillary-pore size.

2. SiO_2 gels have very small capillaries whose radii, according to Freundlich,[13*] range from 12 to 30 Å. The minimum rather than the maximum is critical for the diffusion, hence no diffusion occurs.

3. Diffusion of small-sized micelles can occur, but only at a very slow rate because of the inherently low value of D and the great impedance offered by the gel structure. Friedman and Kraemer[16*] gave the pore radii of 5-percent gelatin as 47 to 57 Å. It seems probable that 1-percent agar has the same size of capillaries as 5-percent gelatin, judging from the diffusion rate of O.M. sols in the two media. Friedman[15*] gave values of 7 Å for the pore radii in 5-percent agar and 29 Å for those in 2-percent agar. From a rough extrapolation of these data, the value of about 50 Å suggested above for the capillary radii in 1-percent agar seems to be a reasonable value.

The conclusion is obvious that the diffusion of colloidal particles in most soil systems is sharply limited. In the first place, soil systems represent gels of rather high concentration in comparison with those used here. Nor can much importance be attributed to diffusion rates of less than 1 mm. per week in soils where conditions that induce flocculation occur with great frequency. Desiccation by evaporation in the summer and by freezing in the winter recurs at short intervals. Thus the movement of materials in the sol form must be chiefly by convection in water percolating thru the pores of sands, or down the crevices between the structure particles in heavier soils. This would explain the accumulation of colloidal matter in the lower horizons on the faces of structure particles and in old root channels and worm holes thru which percolating waters readily find their way.

The formation of concretions, often found embedded within massive soil material where no entering channels are discernible, is not easily accounted for in this manner. It cannot be assumed that the concretions were formed prior to the accumulation of the clay in the profile, that is, while the parent material was still friable and porous, for observations on concretion occurrence[55*] have shown them to be more numerous in the older soils. The more probable explanation is that the concretions resulted from the movement of soluble forms of iron that would not be impeded by the small size of the pores in the soils.

DIFFUSION OF SOLUBLE FORMS OF IRON

The study of the diffusion of soluble materials was limited to the investigation of iron for the following reasons: (1) iron is a major constituent of enrichment in the concretions found thruout the profile of podsolic soils; (2) it is relatively easy to detect iron in small quantities colorimetrically; and (3) the properties of iron are similar enough to those of manganese, the other major constituent of enrichment, for the behavior of the iron to be indicative of the behavior of the manganese.

Iron, either ferrous or ferric, may be present in solution as a cation, as part of an un-ionized molecule, or as a constituent of a complex anion. Frequently more than one form is present in a given system. Since these diffusing units are molecular or smaller, the size of particle would not tend to restrict movement in gels, tho it might affect the rate of diffusion somewhat. The critical factor in limiting diffusion should be interaction with the gel medium. For example, gels of high pH might inhibit diffusion of ferric ions by causing their precipitation as the hydroxid.

The effect of concentration on diffusion rate cannot be disregarded here, as it was in the case of sols in which concentrations were all very small and the rates so slow that the concentration gradient changed but little. The concentration gradient is one of the factors in Fick's law of diffusion[30*] expressed by the following equation:

$$dm = Dq\frac{dc}{dx}dt$$

where m is the amount of material diffusing, D the diffusion constant, q the cross-section, c the concentration, x the distance, and t the time. From this equation it is evident that the concentration gradient dc/dx is an important factor in determining the rate of diffusion. Because it was not possible to maintain a uniform concentration in all systems in these tests, observed differences in rate of diffusion will be considered significant only when they are of different orders of magnitude.

The gels for the following experiments were prepared in the same manner as previously described for the study of sol diffusion. Behavior of the several forms of iron is discussed separately.

Cathodic Iron

Diffusion in Sols.—Ferric chlorid and ferrous sulfate both diffused readily in agar and bentonite, but the ferric salt was impeded

somewhat in gelatin. The data are presented graphically in Fig. 3, along with the data for the O.M. sol studied previously (page 108), in order to compare its rate with those for molecules and ions. The diffusion of $FeCl_3$ can be observed readily at moderate concentrations by the color imparted to the gel by the ferric ion. Since the ferrous

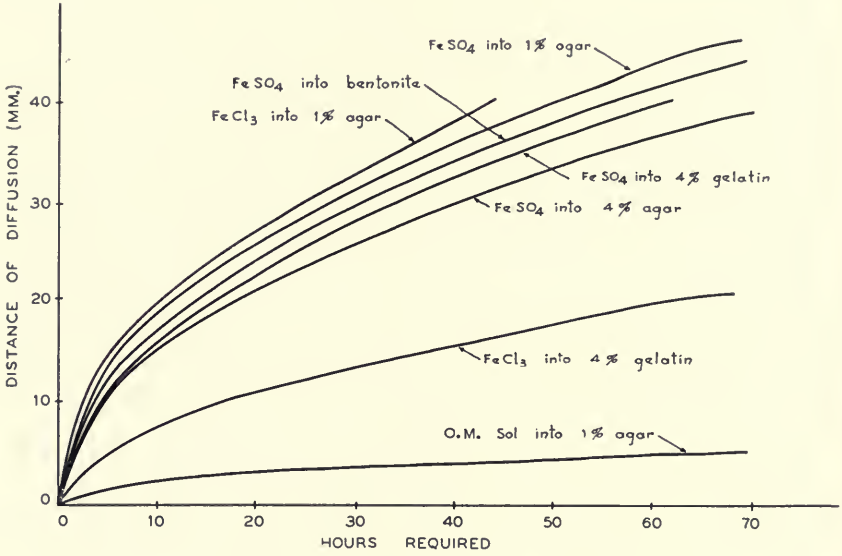


FIG. 3.—RATE OF DIFFUSION OF IRON SALTS AND OF O.M. SOL INTO VARIOUS GELS

ion is colorless, its movement was detected by adding a trace of $K_3Fe(CN)_6$ to the gel. The formation of Turnbull's blue after such addition signifies the presence of Fe^2 ions. Similarly $K_4Fe(CN)_6$ will form Prussian blue with Fe^3 ions, and thus permit their detection at concentrations too low for the observation of the color due to Fe^3 ions alone.

No significant differences in rate were observed in the diffusion of the iron salts in agar and bentonite. Increasing the concentration of agar to 4 percent, which makes an extremely rigid gel of small pore size, had but a slight retarding effect. As predicted, therefore, these ions and molecules are so small in relation to the capillary-pore size of the gels that mechanical hindrance is unimportant.

The effect of the concentration gradient is illustrated by the change in slope of the curves with advancing time (Fig. 3), particularly

noticeable near the 10-hour interval. The solution of the salt is progressively diluted the farther it diffuses into the gel, and consequently the rate at which the boundary continued to advance decreased considerably. In contrast the rate of diffusion for the O.M. sol was nearly constant, since but slight differences in concentration gradient occur with lapse of time.

In gelatin the diffusion of $FeCl_3$ was retarded, as mentioned above, and the gel assumed a deep red color to the depth of salt penetration. This color, unlike the yellow appearance of agar and bentonite into which $FeCl_3$ had diffused, suggests that the salt and gelatin react with a consequent hindering of diffusion. No reaction between $FeSO_4$ and gelatin was indicated either by color or by variations in the rate of diffusion (Fig. 3).

Effect of pH on Diffusion.—Tubes containing 8-percent gelatin at pH 4.0, 5.0, and 6.0 were prepared. The rate of diffusion of $FeCl_3$ was the same at all pH values, and the color developed likewise was red (Fig. 4). The experiment was repeated with a series of gels to which a little $K_4Fe(CN)_6$ had been added. Most rapid diffusion then occurred at pH 4.0 with progressively decreasing rates at 5.0 and 6.0.

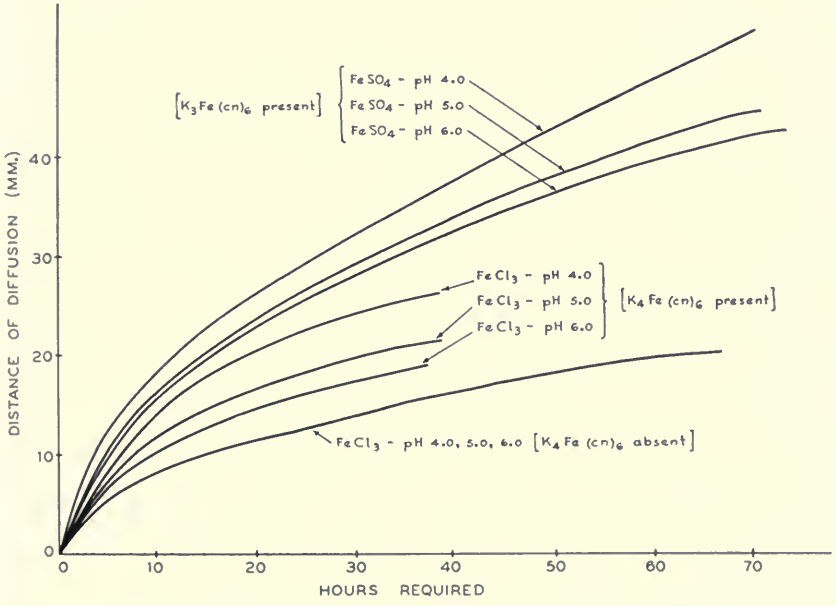


FIG. 4.—RATE OF DIFFUSION OF $FeSO_4$ AND OF $FeCl_3$ INTO GELATIN AT DIFFERENT pH VALUES

No red color was observed, but the intensity of the Prussian blue was strong at pH 4.0 and very weak at pH 6.0, indicating that less iron was moving thru the gel at the higher pH values. As the graph shows, all rates were higher than where $K_4Fe(CN)_6$ was absent.

The diffusion rate of $FeSO_4$ was also found to vary slightly with varying pH, using the same series of gelatin gels (Fig. 4). Again the amount of iron moving as measured by the intensity of Turnbull's blue decreased greatly with rising pH. Before discussing these data, however, it will be helpful to consider the solubility of iron as it is affected by the pH of the solution.

Solubility.—Halvorson and Starkey[20*] have calculated the solubility of ferric iron at various pH levels, using data they obtained on the conditions of equilibrium in solutions containing ferrous sulfate and

TABLE 2.—SOLUBILITY OF FERRIC IRON

pH of solution	Fe^3 in solution[a]	Fe^3 in Knop's solution[b]
	ppm.	*ppm.*
3.0	6.1	.....
3.3	.....	.1
4.0	6.1×10^{-2}	5×10^{-2}
5.0	6.1×10^{-5}	2×10^{-2}
6.0	6.1×10^{-8}	3×10^{-3}

[a]As calculated by Halvorson and Starkey.[20*] [b]As determined by Olsen.[45*]

ferric hydroxid. Olsen[42*] made a direct determination of the Fe^3 in Knop's nutrient solution at varying pH values. The data of those two studies (Table 2) are in good agreement up to pH 4.0, and they show that at this reaction (pH 4.0) the solubility of Fe^3 is vanishingly small. The divergence of the two sets of data at pH 5.0 and above can be attributed to the presence of phosphates in Knop's solution. Smythe and Schmidt[49*] have shown that iron forms anodic complexes with phosphates and will not precipitate normally in their presence.

The solubility of ferrous iron is difficult to evaluate unless the oxidation-reduction potential of the solution is known in addition to its pH. At even moderate oxidation-reduction potentials Fe^2 slowly changes to Fe^3 with a consequent decrease in solubility. The amounts of cathodic Fe^2 that should be in solution at definite pH values have been calculated by Halvorson and Starkey,[20*] assuming the solution to be in equilibrium with the O_2 of the atmosphere. Cooper[8*] gives much lower values for the amount of iron dissolved in sea water (Table 3). He points out, however, that at lower oxidation-reduction potentials

TABLE 3.—SOLUBILITY OF FERROUS IRON

pH of solution	Fe^2 in solution[a]	Iron dissolved in sea water[b]
	ppm.	*ppm.*
3.0	270	.....
4.0	2.7	.....
5.0	2.7×10^{-2}	.....
6.0	2.7×10^{-4}	5×10^{-6}
7.0	2.7×10^{-6}	4×10^{-8}

[a]As calculated by Halvorson and Starkey.[20] [b]According to Cooper.[7]

considerably more iron will be in solution. It cannot be concluded that any one of these values applies to a given situation unless it can be shown that the equilibrium between Fe^2 and Fe^3 has been attained. However, the data are, in general, indicative of the solubility to be expected in the gel systems when they have been exposed to the atmosphere.

Discussion.—In view of the solubility relationships outlined, the fact that diffusion was observed in the gels at pH 6.0 might be attributed to hydrolysis of the iron salts with consequent lowering of the pH of the media. That this actually occurred may be inferred from the gradual appearance of a brownish precipitate of ferric hydroxid at the surface of the gel systems to which iron salts had been added. The brown color observed in the tubes containing $FeSO_4$ is easily explained by the oxidation of Fe^2. Demolon and Batisse[10] observed the hydrolysis and precipitation of iron salts that they attempted to percolate thru columns of neutral soil, which in effect would be comparable to a gel of pH 7.0.

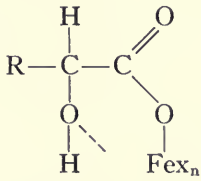
When the pH is low it can be concluded that soluble salts yielding ferrous and ferric ions readily diffuse in all the gels used except gelatin, which medium causes some retardation in the diffusion of the ferric ion. At higher pH values such as might be encountered in ordinary soils, considerable interference with diffusion was encountered. This interference might be attributed to the low solubility of iron under these conditions. Because the effects of hydrolysis tended to obscure the results, a more definite statement cannot be made.

Hydrolysis effects can be eliminated entirely by using nondissociated iron compounds to determine the diffusion in neutral media. It is also possible to use a dissociable iron compound whose anion is so insoluble that hydrolysis effects and consequent pH alteration will be very small; in this manner, the effect of pH on the diffusion of cationic iron can be determined.

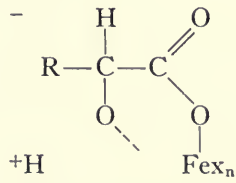
Anodic Iron

A number of iron compounds which yield no ferrous or ferric ions in solution are known, a familiar example being $K_3Fe(CN)_6$. Certain organic acids and proteins are very effective in preventing the ionization of the iron combined with them, as has been shown by Smythe and Schmidt,[49*] who studied both the amount of iron bound by the various materials and the electrophoretic behavior of the resulting iron complexes. Among the organic acids they found that those containing an alpha hydroxyl group (one adjacent to the carboxyl group) were most effective in preventing the ionization of iron. Thus, hydrocrylic acid (CH_2OHCH_2COOH) was able to bind much less iron than lactic acid ($CH_3CHOHCOOH$), and the dicarboxyl acids were more effective in this respect than the monocarboxyl acids.

The electrophoretic behavior of the organo-iron complexes depended on both the pH and the acid used. Iron in lactic acid, for example, moved to the anode only when the pH was above 7.0, whereas in tartaric acid it moved to the anode even at pH 2.1. Smythe and Schmidt[49*] explained this "anodic" behavior by assuming that secondary or coordinating valence forces acted on the iron as follows:



This secondary attraction of the Fe for the hydroxyl group facilitates the ionization of the hydrogen, thus:



The entire resulting anion, including the iron, can now move to the anode. This hypothesis of the binding of the iron by organic acids is in accord with the recent theory of chelate ring structure as summarized by Diehl.[11*]

In the soil, iron would form anodic complexes, principally with portions of the organic matter, since other chelating materials are not

present in appreciable quantity. Oden[41*] isolated so-called humic acids from soil organic matter and found that in spite of their colloidal nature their chemical properties in general correspond to those of the simple organic acids. Since then, Mitchell[38*] and others have shown that lignin-like compounds are the important constituents of soil humus. Tho the exact structure of lignin is uncertain, it is known to resemble that of the pentosans and hence humic acids must contain hydroxyl as well as carboxyl groups. Thus chelated iron-humus complexes should exist in soils.

Preparation of Anodic Iron Complexes.—To 50 ml. of O.M. Sol 1 was added .5 ml. of N/10 $FeCl_3$. Partial flocculation occurred within a short time. Only a slight color was obtained either with KCNS or $K_4Fe(CN)_6$, indicating the greatly repressed ionization of Fe^3. However, when a portion of the sol was treated with H_2O_2, KCNS gave a distinctly red color, showing that the iron bound by the organic matter was set free on its oxidation. Acidification with HCl also released enough Fe^3 to give a good color test with KCNS.

A ferrous humate complex was prepared by adding 20 mg. of $FeSO_4$ to 200 ml. of the same O.M. sol. After standing overnight the complex showed no flocculation, and only a slight color developed on the addition of $K_3Fe(CN)_6$. After treatment with either H_2O_2 or HCl as above, a distinct test for Fe^2 was obtained.

From the behavior of these complexes and the postulated structure of humus, it seems highly probable that the ionization of the iron is repressed by the formation of chelate rings as outlined by Smythe and Schmidt[49*] for the organic acids. This same conclusion was reached by Dyer and McFarlane.[12*] Because the organic acids give colorless systems in which such complicating factors as flocculation are eliminated, they were used instead of the humic materials for the study of anodic iron diffusion in these experiments.

Other complexes were formed by adding $FeSO_4$ to an excess of citric and tartaric acids in separate flasks. From this mixture is obtained a clear solution which gives a blue color upon the addition of $K_3Fe(CN)_6$. Neutralization with NaOH caused color in the solution—at pH 7.0 a distinctly yellowish tinge. No precipitation of iron occurred. As the pH was raised the test for Fe^2 became continually more faint. The stability of the system was shown by the failure of iron to precipitate even at pH 10.0.

Diffusion Experiments and Technics.—Aliquots of the electrodialyzed bentonite sol were placed in separate flasks and the pH adjusted to the desired value with $Ca(OH)_2$. The resultant sols were

allowed to stand several days to reach equilibrium before making the final pH measurements, and the gels were then prepared by centrifuging the sols as previously described (page 105). The pH of the gel systems was probably somewhat lower than that of the sols used in their preparation: when a 1.7-percent bentonite sol of pH 3.5 was diluted to twice its volume with distilled water, the pH of the diluted system was 3.8. The ratio of concentrations of sol and gel was always less than 1:2, hence there should be but slight change in the pH of the system after centrifuging.

Ferrous citrate and tartrate complexes were placed on bentonite gels prepared from sols of pH 5.0 and 10.0. That diffusion occurred in both cases was indicated by a diminution of the intensity of the yellow color of the complex solution on the gel. The entire absence of any brownish precipitate in the gel such as was observed when $FeSO_4$ diffused in bentonite, is evidence of the stability of the iron complexes at these widely different pH levels.

To demonstrate the presence of iron in the gel system, it is necessary to alter the usual technic of the $K_3Fe(CN)_6$ color test. As was shown above with the ferrous humate complex, it is necessary either to acidify the complex or to destroy the organic portion with H_2O_2 in order to obtain any appreciable concentration of Fe^2 ions in solution. Furthermore at about pH 6.5 and above, Turnbull's blue does not form, hence no test for Fe^2 with $K_3Fe(CN)_6$ can be made except in acid solution. The addition therefore of a few drops of HCl to the system will both change the iron to the cathodic form and permit the development of the blue color where the iron is present.

The method used permitted the test for iron to be made without affecting the previous course of diffusion. The gel was prepared in a tube open at both ends, one end being closed with a special stopper that would not break the tube in the centrifuge. The stopper was kept in the lower end until diffusion had progressed for the desired time. Then it was removed, the tube inverted, and the acid added and allowed to diffuse thru the gel. The $K_3Fe(CN)_6$ could also be added at this time instead of during gel preparation. Where the acid and ferricyanid meet the diffusing iron complex, a blue boundary appears.

By this procedure iron was shown to have diffused into both gel systems used (of pH 5.0 and 10.0, respectively), confirming the observation made above on the color changes in the solution of the diffusing complex. Because the iron is released very slowly by the acid, the rates of movement could not be ascertained accurately, but they were of the order of 1 cm. per day or approximately half that for $FeSO_4$.

Application to Soil Systems.—That iron may diffuse in neutral and alkaline soil systems in the anodic form is undoubtedly implied by the results of these experiments. The organic matter in the soil contains substances, principally in the humic portion, that may function in the same capacity as tartaric acid. However, diffusion of ferrous-humate complexes should be at least as slow as that of the O.M. sol (Fig. 3) since that type of humus will constitute the bulk of the material available for complex formation. The simpler organic acids that would diffuse more rapidly are almost entirely absent from soils because of their great susceptibility to destruction by microorganisms. Ferric-humate complexes would have a very restricted diffusibility because of their tendency to flocculate.

Surface Effects in Diffusion

Many silicate minerals contain iron in the ionic state as a constituent of the crystal lattice.[43, 44*] Kelley and Jenny[28*] have shown that when minerals are ground in a ball mill, the lattice structure is so broken up that many of the basic ions are exposed and behave much as do the exchangeable ions of clays. In contact with a suitable type of gel, then, the iron in the ground mineral should exchange with the cations of the gel. Iron from this source should be entirely free of soluble anions.

Gels composed of amphoteric colloids should not be suitable media for the study of diffusion of iron from a silicate. In the first place, the amphoteric materials have cation exchange capacity only when above their isoelectric point. Secondly, many amphoteric gels are organic and would be expected to repress ionization in the manner described in the discussion of anodic iron. Bentonites, which have no isoelectric point and are themselves silicates, should be very satisfactory gel media in which to study the diffusion of iron from silicates.

Preparation of Silicate Sources of Iron.—The ferrous-iron-bearing minerals that were used were hornblende, olivene, chlorite, serpentine, and orthoclase. Orthoclase should contain but a trace of Fe^2. Epidote was the only mineral selected that contained much ferric iron. Samples of each were crushed in a mortar by hand and then ground for a week in a rubber-lined ball mill with agate balls. A very fine impalpable powder was obtained in each case.

An iron bentonite was also prepared by adding clean iron filings to an aliquot of the 4-percent electrodialyzed sol. Hydrogen was slowly evolved and appeared as small bubbles in the sol. After a week the

reaction had practically ceased and the pH had risen from 2.8 to 5.4. The resultant sol gave a strong test for Fe^2 with $K_3Fe(CN)_6$, but there was no reaction with KCNS.

Diffusion of Ferrous Iron From Silicates in Acid Bentonite.— Powdered hornblende was sprinkled on top of a bentonite gel which contained a trace of $K_3Fe(CN)_6$. To prevent drying of the gel, it was kept covered about 1 cm. deep with water. Within a few minutes a blue color appeared at the gel surface where the powder rested and then slowly advanced thru the gel, indicating the release and diffusion of Fe^2. Similar experiments with olivene, serpentine, and chlorite gave similar results.

In another experiment a small quantity of iron bentonite was carefully introduced at the bottom of a tube, then centrifuged and the supernatant liquid decanted. The inner walls of the tube were cautiously rinsed before some H-bentonite sol was added on top. The tube was again centrifuged, giving a sharp contact between the H- and Fe-bentonite gels. $K_3Fe(CN)_6$ was added to the surface. The next day a blue ring had formed near the center of the uppermost gel of H-bentonite, marking the region where the Fe^2 ions diffusing up from below had encountered the downward-moving ferricyanid.

Thus the expectation that both minerals and bentonites carrying ferrous ions on their surfaces can serve as sources of iron for diffusion in bentonite gels was fulfilled.

The rates of diffusion of iron from hornblende and olivene are plotted in Fig. 5. With serpentine and chlorite, the rate of diffusion of Fe^2 was approximately the same as with hornblende. However, when orthoclase was used the rate was much slower. Since the concentration gradient is very important in determining the rate, it is probable that the differences in rate were due either to variation in the iron content of the minerals, or to the relative ease of its release, or to both.

Diffusion of $FeSO_4$ was two to three times faster than the diffusion of iron from the silicates (Figs. 3 and 5). Again, since the concentration gradients are unknown, it is not safe to generalize. The rates were all of the same order of magnitude, however, indicating that the diffusing particles were of ionic or molecular size in both cases.

In a further experiment an electrodialyzed sol of bentonite (Sol 2) from another source was prepared, having a pH of 3.0 and a concentration of 1.5 percent. The gel obtained by centrifuging this sol at the same speed as previously had a concentration somewhat less than 2 percent, as compared to 5 percent for the gel from the other ben-

tonite, Sol 1. When powdered chlorite was added to the 2-percent gel, diffusion of iron occurred as in the 5-percent bentonite, but at a somewhat slower rate. This rate differential will be referred to later (page 135).

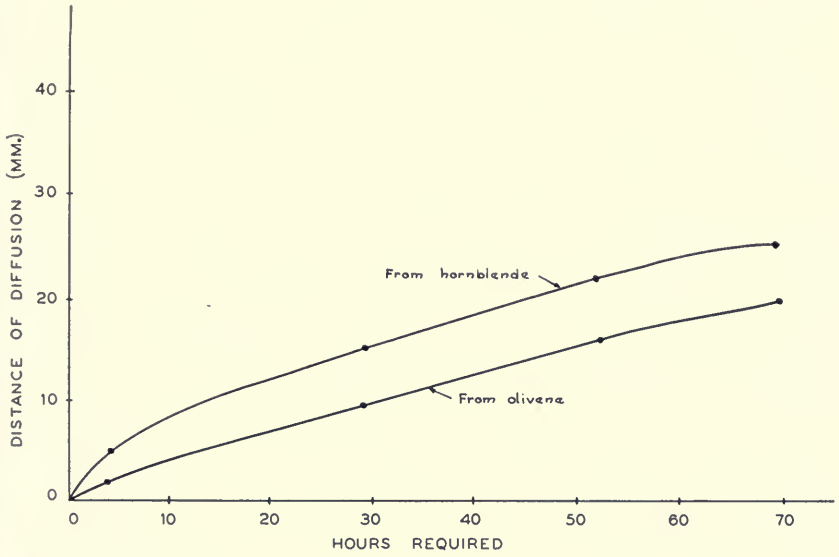


FIG. 5.—RATE OF DIFFUSION OF FERROUS IONS FROM POWDERED MINERALS INTO BENTONITE GELS

Diffusion of Ferrous Iron From Silicates in Other Media.—Hornblende, chlorite, and olivene were placed on agar gels and the systems tested for the presence of ferrous iron at intervals up to a month. No diffusion was detected. Egg albumen gels gave similarly negative results. The mineral powders remained unchanged in appearance, a fact that is significant in view of the following observation.

Some hornblende and olivene powders that had been allowed to remain in contact with bentonite gels for two to three weeks were noticed to have acquired a fluffy and flocculent appearance. When the tubes were disturbed or agitated slightly, the fluffy aggregates readily became suspended in the supernatant liquid, quite in contrast to the behavior of the fresh powder, and of that in contact with the agar and albumen gels. It was further noted that the blue color on top of the gel had faded to a depth of several millimeters. This can be explained by the exchange of Ca and Mg ions of the mineral powder for

the H ions of the bentonite. The consequent rise of pH in the bentonite would decompose Turnbull's blue, as mentioned previously (page 124). A drop of HCl soon restored the color, verifying this hypothesis.

The interpretation of the above observations is that during exchange of the basic ions, including Ca and Mg as well as Fe, for the H ions of the bentonite, the mineral powder is "weathered" and becomes in part colloidal. The failure of this change to occur in minerals on the agar and albumen gels is evidence of the absence of ionic exchange, which is a prerequisite for diffusion of Fe from minerals. An hypothesis for the inactivity of mineral powders on organic gels has already been suggested (page 122).

Diffusion of Ferric Iron From Silicates.—Two sets of bentonite gels were prepared, one containing KCNS and the other $K_4Fe(CN)_6$. Powdered epidote failed to produce a coloration in either system. Small quantities of ferric iron are usually present in hornblende and olivene, and these minerals also were tried with the above gels. They behaved as did epidote, giving no color with either reagent.

The failure to obtain a color test for Fe^3 in these experiments may have been due to causes other than the absence of Fe^3. Prussian blue forms only in acid solutions because of the low activity of Fe^3 ions in solutions above pH 4.0. The Ca and Mg ions exchanged would soon raise the pH above this value, at least near the mineral powder. Furthermore, the use of nonaqueous solvents in connection with Comber's thiocyanate soil-acidity test indicates the special care that must be taken in order to detect Fe^3 with KCNS even in moderately acid media.

The obvious expedient of acidifying the gel before testing for Fe^3 is subject to serious criticism because of the ease with which Fe^2 changes to Fe^3. Simon and Haufe[48*] have shown that even $K_3Fe(CN)_6$ will oxidize considerable quantities of Fe^2. Thus a positive test for Fe^3 on acidification could not be interpreted as definite evidence of its diffusion, since the iron might have moved in the ferrous state and then have been oxidized to Fe^3.

Because of such uncertainties no further study was made of the diffusion behavior of Fe^3. However, the strong adsorption of trivalent ions, which according to Thomas[51*] is often so great as to cause reversal of charge of colloidal particles, suggests that exchange of Fe^3 ions from silicates may be so hindered as to largely eliminate the possibility of their diffusion.

Anions Associated With Iron in Diffusion.—The long period of dialysis undergone by the bentonite sols should have removed all their

diffusible anions. Certain anions that could diffuse with the iron might, however, gain access to the systems from the air, or during the addition of the minerals and the indicator $K_3Fe(CN)_6$.

That $K_3Fe(CN)_6$ is not concerned in iron diffusion was shown by the formation of a blue ring within the acid bentonite (page 126). To further verify this point, hornblende and olivene were added to bentonite gels containing no $K_3Fe(CN)_6$. After a day, the minerals were carefully washed off, as well as about 2 mm. of the gel surface, and $K_3Fe(CN)_6$ added. A blue color immediately developed at the surface and rather soon reached approximately the same depth as had been previously observed for the diffusion of iron in those gels that had $K_3Fe(CN)_6$ added during their preparation.

In an experiment to discover whether CO_2 is associated with iron diffusion some bentonite sol was gently boiled for several hours to remove CO_2, and precautions were taken to restrict access of air to a minimum during preparation of the gel and addition of the hornblende. Diffusion of the iron occurred at the same rate as in the unboiled bentonite gels. Complete removal of CO_2 probably was not secured, but the quantity remaining must have been negligible. Thus, while not conclusive, the experiment suggested that CO_2 is not associated with the iron during diffusion.

To determine the possibility of anion contamination from the mineral powder, a small amount of hornblende was thoroly mixed with bentonite Sol 1 and allowed to stand overnight. The sol was then centrifuged and the supernatant liquid decanted. Any diffusible anions should have been present in the solution so obtained, along with an equivalent number of cations such as Fe and Ca. Before a conclusive test for ions could be made, however, the total absence of colloidal particles had to be ascertained by examination in a Tyndall beam. Small quantities of bentonite remaining in suspension could be flocculated with a little $AlCl_3$, and then removed by centrifuging. $Ca(OH)_2$ is slightly less effective, but must be used when chlorids are to be determined.

Several aliquots of the clear supernatant liquid so obtained from the hornblende-bentonite mixture were treated with $K_3Fe(CN)_6$, $BaCl_2$, and $AgNO_3$. No color or precipitate was obtained with any reagent, thus showing the absence of Fe^{++}, SO_4^{--}, and Cl^-. If other diffusible anions were present, then, as stated above, Fe^2 ions should have been present in the supernatant liquid in association with them.

The conclusion tentatively reached on the basis of the above data is that the chief anions associated with the iron in the course of dif-

fusion are the negatively charged colloidal particles of bentonite. The movement of the iron might then be largely over the surface of the colloids rather than thru the free solution. The mechanism involved can be more satisfactorily discussed after consideration of diffusion in neutral and alkaline media.

Diffusion at Higher pH Levels.—According to the literature already cited, the solubility of cathodic iron above pH 6.0 is extremely low. Usually the assumption can be safely made that solubility is a prerequisite for diffusion. However, if surface movement in certain gel systems is possible, then solubility in the ordinary sense may not be a factor when dealing with these systems. In view of these facts, if diffusion of iron could be demonstrated in the pH range where its solubility is negligible under ordinary circumstances, it would constitute a compelling argument in favor of a surface hypothesis.

Certain difficulties are met in observing the diffusion of iron at pH values above 6.0. The most serious is the failure of Turnbull's blue to form, and if its does form, the decomposition of it by alkaline solutions, as mentioned previously (page 124). This problem can be met by acidification after diffusion has progressed for the desired interval. Another difficulty is that some bentonites contain Fe^2 in the lattice that is released by HCl. Therefore it is desirable in many instances to have a blank consisting of the same gel to which no mineral has been added, in order to compare the relative intensities of color developed. If, however, the observations can be so timed that a blue ring is formed within the gel, as was the case with the anodic iron experiments, (page 126), then the evidence for diffusion is conclusive without the use of a blank.

The pH of four aliquots of bentonite Sol 1 was adjusted with $Ca(OH)_2$ to 5.1, 6.8, 7.1 and 8.0 respectively, and gels prepared therefrom in tubes open at both ends as previously described. Hornblende and a trace of $K_3Fe(CN)_6$ were added to the surface of each. Color developed only in the first tube (pH 5.1), the others remaining white. After five days the tubes were inverted and HCl added, whereupon a blue color also developed in the systems of pH 6.8 and above.

The experiment was repeated using aliquots of bentonite Sol 2 adjusted to pH 6.8, 8.6, and 11.0. Duplicate gels were prepared from each aliquot and powdered chlorite added to one, the other being used for a blank. After a week, the tubes were inverted and HCl and $K_3Fe(CN)_6$ added. Only a faint coloration was produced in the blanks, while a moderately strong blue appeared in each system where chlorite was present. The depth of color penetration was less than in

the acid bentonite with which chlorite had been in contact for the same period, a fact which suggests that the rate of diffusion was slower at higher pH levels.

To get a better idea of the rate of movement, a series of four tubes was prepared, each tube containing two layers of gel, the lower one being prepared from the Fe-bentonite sol of pH 5.4 and the upper one from an aliquot of bentonite Sol 1 that had previously been adjusted to pH 6.4 with $Ca(OH)_2$. HCl and $K_3Fe(CN)_6$ were added to successive tubes at 2-, 3-, 4-, and 7-day intervals. Blue rings formed within the Ca bentonite gels in each tube at increasing distances from the plane of contact between the gels. These distances were respectively 6, 8, 9, and 10 mm. Thus the rate of diffusion of iron at pH 6.4 is about half that at pH 2.8 (Fig. 5). As has been pointed out (page 126), however, the significance of variations in diffusion rates, when within the same order of magnitude, is very uncertain under the conditions of these studies.

It must be concluded from the above data that the diffusion in bentonite of iron from silicates is independent of pH, tho the rate may be affected thereby. The significance of this statement with respect to the mode of diffusion will be more apparent after a reconsideration of iron solubilities.

Solubility of Ferrous Iron.—The data quoted on the solubility of ferrous iron as a function of pH (Table 3) assumed equilibrium with the oxygen of the air. As was suggested (page 120), such equilibrium may very rightly be questioned because of the slow rate of oxidation of Fe^2. A greater solubility of iron than the data indicated might thus occur at times in the bentonite systems. Because of this uncertainty as to the equilibrium status, it is proposed to calculate the solubility of ferrous iron in an O_2-free system, in which the maximum solubility of iron is to be expected.

The two anions, aside from the colloidal particles themselves, most likely to occur in the bentonite systems are OH^- and CO_3^{--}. The value suggested by Cooper[7*] as most probable for the solubility product of $Fe(OH)_2$ is 3.2×10^{-14}. At pH 9.0, the concentration of the OH ion is 10^{-5}, thus

$$3.2 \times 10^{-14} = [Fe^{++}]\,[OH^-]^2 = [Fe^{++}]\,(10^{-5})^2$$

whence,

$$[Fe^{++}] = 3.2 \times 10^{-4} \text{ mol/L.}$$

This value corresponds to 170 ppm. of iron. In a similar manner, the solubilities at pH 10 and 11 are found to be 1.7 and .017 ppm. of iron.

Thus only in solutions below pH 10 may an appreciable concentration of $Fe(OH)_2$ exist, even in oxygen-free solutions.

It is highly probable that the bentonite sol was in equilibrium with the partial pressure of the CO_2 of the air, for which 3×10^{-4} atmosphere is a conservative figure. Latimer and Hildebrand[31*] give the solubility in water of CO_2 when its partial pressure is one atmosphere as 3.4×10^{-2} mol/L. Thus at a partial pressure of 3×10^{-4} the amount of CO_2 in solution will be

$$3.4 \times 10^{-2} \times 3 \times 10^{-4} = 10^{-5} \text{ mol/L.} \quad (1)$$

Also according to Latimer and Hildebrand the ionization constant for the first H ion of H_2CO_3 is

$$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = 3.5 \times 10^{-7} \quad (2)$$

and for the second H ion

$$\frac{[H^+]\,[CO_3^{--}]}{[HCO_3^-]} = 3.7 \times 10^{-11} \quad (3)$$

Multiplying these two equations, (2) and (3), gives

$$\frac{[H^+]^2\,[CO_3^{--}]}{[H_2CO_3]} = 13 \times 10^{-18} \quad (4)$$

From equation (1) above, $[H_2CO_3] = 10^{-5}$ mol per L. Substituting this value in equation (4), the equation then becomes

$$[H^+]^2\,[CO_3^{--}] = 13 \times 10^{-23} \quad (5)$$

Above a certain pH the H_2CO_3 will be completely ionized, that is

$$[CO_3^{--}] = 10^{-5} \text{ mol per L. (Equation 1, above)}$$

Substituting this value in equation (5)

$$[H^+]^2 = 13 \times 10^{-18}$$

and $$[H^+] = (13 \times 10^{-18})^{1/2} = 3.6 \times 10^{-9}$$

or $$pH = 8.4$$

Above this pH value the H_2CO_3 is completely ionized and the CO_3 ion concentration will therefore be equal to the concentration of the CO_2 in solution, namely, 10^{-5} mol/L. The solubility product given by

Curtman[9*] for $FeCO_3$ is 2.5×10^{-11}; hence the concentration of the Fe^2 ion that can exist in the bentonite systems above pH 8.4 will be 2.5×10^{-6} mol/L, which is equivalent to .14 ppm. of iron. This calculated value agrees well with the solubility values for $FeCO_3$ assembled by Mellor,[36*] approximately .1 ppm. at pH 8.4. Thus, between pH 8.4 and about 10.5, it will be the solubility of $FeCO_3$ rather than that of $Fe(OH)_2$ which will restrict the amount of iron in solution.

A solubility of .14 ppm. seems entirely too small to cause a measureable amount of iron diffusion, particularly since the concentration of Fe^2 must approach .5 ppm. in order to be detected with $K_3Fe(CN)_6$. How then can a sufficient concentration gradient of Fe^2 ions exist above pH 8.4 to account for the diffusion observed? The following paragraph suggests that an hypothesis of surface diffusion is adequate to explain the behavior of the iron under these conditions.

Abramson[3*] has presented Gouy's concept of the diffuse ionic atmosphere about colloidal particles and pointed out its similarity to the more recent Debye-Hueckel ionic-attraction theory for strong electrolytes. In both cases the predicted result is an increased concentration of ions of unlike charge in the vicinity of the charged particle and a decreased concentration of ions of like charge. The concentration differentials are greatest at the particle surface and fall off exponentially with the distance from the surface. A quantitative evaluation of the decrease in anion concentration to be expected at the negative bentonite surface is too complex to be attempted here, but the qualitative picture indicates that anion activity within the double layer may be several magnitudes less than such activity in the outer liquid. That is to say, the pH of a sol does not indicate what the OH ion activity within the double layer might be. Therefore the solubility calculations do not apply to the region of the ion atmosphere, and while the Fe^2 ions remain within this region, their activity may greatly exceed that which would be possible beyond the double layer.

Thus by assuming two-dimensional diffusion on the surfaces of the bentonite particles, it is possible to account for the movement of iron at high pH levels. The fact that no iron was found in the solutions separated by centrifuging from the bentonite sols known to have ferrous ions on their surfaces (page 129) indicates that the iron moves by surface diffusion in the acid bentonite gels also.

Theory and Mechanism of Surface Diffusion

Before considering the probable mechanism of surface diffusion, it is desirable to review the important properties of bentonite gels,

including the structure of the individual bentonite particles and the arrangement of these particles in the gel system.

Marshall[35*] has summarized the modern conception of clay particles in terms of a layer lattice of tremendous effective surface. The model proposed for bentonite, which also fits the soil clays, assumes platelike particles of essentially two-dimensional character having on their surfaces exchangeable ions which balance the residual charges in the lattice. The calculation of Paver and Marshall[45*] for the concentration of exchangeable ions between two adjacent surfaces of bentonite gives a value of 2.5 N, indicating the close proximity of the "exchange spots" on the surfaces.

Studies of the gelation of bentonite by Houser and Reed[24*] confirm the previous conception that this gel is a two-phase system, both phases of which are continuous. That is, the particles form an irregular network or "brush heap" by which each particle is connected, directly or indirectly, to every other one. Within the meshwork, the water is held by occlusion and hydration as part of the rigid system.

The diffusion process is initiated when the mineral powder containing Fe^2 ions comes in contact with the bentonite gel. In acid bentonites, H^+ will replace the Fe^{++} of the mineral, while in neutral and alkaline bentonites Ca^{++} must predominate in the exchange with Fe^{++}. Once on the bentonite surface, the Fe^{++} is still susceptible to exchange with the ions of adjacent particles. Exchange would thus proceed down the surface much like an ordinary diffusion process except that it is restricted to the two dimensions of each particle surface.

Jenny's[25*] kinetic theory of exchange can readily be adapted to help visualize the process. Consider a single colloidal particle whose plane surface bears ions oscillating about the "exchange spots" with an amplitude proportional to the average kinetic energy. Each ion will occupy a volume the diameter of which corresponds to the average amplitude, and while occupying this volume, it can be considered as adsorbed. Those ions which occasionally acquire energies appreciably greater than the average will leave the "oscillation volume" during each period of vibration. Should a foreign ion penetrate the oscillation volume at that instant, it would replace the original ion and be adsorbed in its place. The replaced ion then becomes a foreign ion until it similarly displaces another.

That such a series of exchanges may at times be largely restricted to ions on the surface seems reasonable. In the first place, the data of Paver and Marshall[45*] cited above suggest that the exchange spots are not far separated. Furthermore, Gouy's theory of the diffuse

double layer predicts both an energy distribution and a positional location of the adsorbed ions appropriate to a surface exchange. Thus, as in any kinetic system, the several ion species adsorbed on the surface of the particle will tend to reach a statistical distribution. Since in a gel the solid particles form a continuous phase, exchange diffusion will in time involve the entire gel system.

The solid-phase pathway for ions would be somewhat indirect and hence rather longer than the more direct liquid-phase pathway. The observed diffusion rate of $FeSO_4$ in bentonite was several times greater than that of Fe from silicates (Figs. 3 and 5). If it is assumed that this rate differential might not be entirely accounted for by variations in concentration gradient, then a portion could well be attributed to the longer pathway involved in a surface diffusion. The fact that the diffusion rate of Fe from silicates increased rather than decreased with the concentration of the bentonite in the gel (page 127) also is significant in this connection.

The occurrence of surface diffusion of atoms and molecules has been suggested by the results of several investigations. Volmer[54*] studied the movement of benzophenone on glass and mica and concluded that the molecules, tho adsorbed on the surface, are able to diffuse much like a two-dimensional gas. He also postulated the diffusion of Hg atoms on Hg surfaces to account for the abnormal rates of crystal growth in preferred directions. Lennard-Jones[32*] approached the diffusion of adsorbed gases over solid surfaces mathematically and arrived at a picture similar in many respects to the one proposed by Jenny[25*] for ions on clays. In a later paper Lennard-Jones and Devonshire[33*] concluded that He atoms should diffuse two-dimensionally on LiF crystals with a hindrance equivalent to but an 8-percent increase in mass as compared to free gaseous diffusion.

Even more suggestive for the problem at hand are some data reported by Bradfield,[5*] who observed the accumulation of bentonite particles at the anode membrane during electrodialysis, a fact since mentioned quite generally by others. He described these accumulations as "Finger-like projections . . . . which tended to bridge across the space between the membranes." When the projections were broken with a glass rod, they fell to the bottom of the vessel and the current density dropped from 220 to 10 M.A. He suggested that there might be considerable conductivity attributable to the ions on the bentonite surfaces, a suggestion which is entirely in harmony with a hypothesis of surface diffusion.

In the same paper Bradfield reported the interaction of Na-benton-

ite sol with CaC_2O_4. Twenty percent of the Na was replaced by Ca from this very insoluble salt. With $BaSO_4$, 21 percent of the Na was replaced from an Na-bentonite sol. It seems logical to attribute the replacement in part to surface exchange and diffusion, since with the minute quantities of Ba or Ca ions that would exist in free solution, the bentonite adsorption isotherm predicts a much smaller replacement.[a]

Implications of a Surface-Diffusion Hypothesis

The justification for any theory should be its usefulness in explaining experimental observations. Therefore a few instances of the application of the surface diffusion concept will now be considered, very briefly.

It is well known that ionic reactions in clay systems require some little time to reach equilibrium. For example, Bradfield[5*] questioned whether equilibrium had been attained in certain of his systems that had stood a week. Bentonites and some soil clays have an expanding crystal lattice that permits ions to penetrate within the particles themselves, as shown by Hofmann, Endell, and Wilm.[22*] Surface diffusion could account for the fact that exchange ions reach these regions of poor accessibility as well as for the relative slowness of the process. Similarly, Lennard-Jones[32*] has suggested that gas molecules penetrate the microfissures of crystal surfaces by a surface diffusion.

The picture of iron assimilation by plants is simplified by the hypothesis of surface diffusion. Kliman[29*] has recently shown that plants utilize only ferrous iron; and, according to Halvorson[19*] biologic activity in conjunction with excess moisture in the soil will give rise to ferrous ions even when the reaction is neutral. Some ions will be adsorbed on the clay surfaces and could then diffuse to the root hairs regardless of the pH. The plants can acquire these ferrous ions by exchange with the H ions produced as a result of CO_2 excretion. The pH of a saturated CO_2 solution is 4.0, according to Latimer and Hildebrand,[31*] and this value can be closely approached at the root surface, according to Truog.[52*]

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[a]Since this bulletin was approved for publication (March 25, 1939), Jenny and Overstreet have outlined a theory of surface migration, very similar to the one presented here, by which they explain their data on contact depletion of mineral ions in barley roots. Certain of their later experiments are comparable to those reported in this bulletin, and it is significant that their results are in harmony with those presented here.—"Cation interchange between plant roots and soil colloids," Soil Sci. **47**, 257-272 (1939); and "Surface migration of ions and contact exchange," Jour. Phys. Chem. **43**, 1185-1196 (1939).

Bray[6*] and others have suggested that mineral weathering occurs in alkaline soils, tho they have postulated no satisfactory mechanism. The data presented here substantiate the fact of alkaline weathering, while ionic movement on the crystal surfaces offers a means of accounting for the change in composition of the primary minerals. Iron and other ions which are exposed on the minerals would diffuse over the surface of the soil gel system to regions of lower concentration. In this way it is possible to explain the occurrence of ferromanganiferous concretions in the deeper horizons that are alkaline in reaction and virtually free of organic matter. No other known mechanism seems adequate to account for iron diffusion under these conditions which permit of no complex anodic formation.

General Discussion of Diffusion of Soluble Iron

From the material presented in the foregoing sections, it is evident that any soluble form of iron may diffuse in gels under appropriate circumstances. The following is a brief review of the conditions essential to diffusion of each form of iron, with some indication of the expected mobility in various soil systems.

Iron Salts.—Inorganic ferric and ferrous salts move readily in the more acid media. In media above pH 4.0, however, ferric salts are too insoluble to diffuse. Few soils have a pH as low as this, hence the diffusion of ferric salts in soils is probably rare.

Ferrous salts are mobile in media above pH 5.0 only when the R-O potential is low and the content of organic matter not very large. Where aeration is good, Fe^2 is changed to Fe^3 and its movement thereby limited, but under extreme reducing conditions an appreciable concentration of the ferrous ion may exist up to pH 7.0. In the presence of organic matter, anodic complexes tend to form when the pH exceeds 5.0, thus removing the ferrous ion from solution. Therefore combinations of pH and R-O potentials permitting ferrous salt diffusion may well be of frequent occurrence in the lower horizons containing little organic matter, but because of the tendency of organic matter to form anodic iron complexes when the reaction approaches neutrality, diffusion of ferrous salts in surface horizons should be restricted to those which are exceptionally acid. Because of the low anion concentration in most soils, it should be emphasized that surface diffusion may also occur simultaneously with ferrous salt diffusion.

Anodic Iron.—Organic iron complexes readily diffuse in neutral and alkaline media, but when the pH is very low, they dissociate, releasing the iron. Assuming that humus is the organic portion of the

complex, then in soils the diffusion of ferric iron complexes may often be of minor importance because of the tendency of ferric iron to flocculate humus sols during complex formation. Movement of ferrohumate complexes, however, will likely be of general occurrence in the biosphere.

Adsorbed Iron.—Fe^3 is excluded from the following discussion because surface diffusion of the ferric ion was not demonstrated, and furthermore its properties suggest such diffusion to be unimportant.

The one outstanding prerequisite for surface migration of Fe^2 seems to be the presence of a gel structure of the bentonitic type. Most soils in the podsolic region contain clays of this type in sufficient quantity to be considered as gels. In addition, however, the surface horizons usually contain organic colloids that form a dark coating particularly noticeable on the faces of structure particles. For reasons already outlined, iron would not be expected to diffuse as a cation over surfaces heavily contaminated with organic matter unless the pH were below 5.0. However, within the structure particles the organic colloids are much less concentrated, as is shown by the lighter color apparent when the particles are crushed. Thus, in surface horizons, while surface diffusion will be inhibited on the external structure faces, it might be expected to occur within the particles. In the deeper horizons the organic content is usually too low to interfere with surface migration. As has been mentioned before, it is difficult to account in any other way for the movement of iron in alkaline soil horizons such as those containing large amounts of $CaCO_3$.

The absence of bentonitic colloids in laterites may be one factor that contributes to the characteristic immobilization of iron in soils of the tropical regions, in contrast to the ready translocation of iron observed in soils of the podsolic region where bentonitic clays are common. Since the author has made no studies of either laterites or lateritic soils, it is unsafe to speculate further on this point.

THE IMMOBILIZATION OF IRON

While it was not the purpose of this study to treat in detail the matter of iron aggregation, nevertheless the aggregation behavior of iron, and some of the problems yet to be solved before a complete understanding of concretion formation is possible, are briefly discussed in the light of the knowledge of the mode of iron migration gained in these experiments.

Precipitation and immobilization of iron in soils results from the

formation of the stable and insoluble hydrated ferric oxids, and concretions should result from any local conditions that tend to convert other iron compounds into this form. Ferric salts are precipitated as the hydroxid whenever the pH exceeds 4.0. Precipitation of ferrous salts, on the other hand, requires either a considerably higher pH, or a high R-O potential to first convert Fe^2 to Fe^3. Anodic iron must first be released from the organic complex, which is most readily accomplished thru biologic activity, tho the low pH at root surfaces (about 4.0) may also be effective. Thereafter it will behave as does other ferrous iron. Adsorbed iron must be exchanged from the surface by cations of the soil solution before it can react with precipitating agents readily.

How to account for the localization of these reactions at concretion centers is a complex problem yet to be solved. A fact that seems of great significance in this regard is the universal presence of manganese oxids in the concretions. It has been suggested that the behavior of manganese may be analogous to that of iron; but further, the manganese may be an important agent in the aggregation of iron because of the ready catalysis of R-O reactions by it. The study of the behavior of manganese in soils may therefore be one approach to the problem of iron aggregation into concretions.

SUMMARY AND CONCLUSIONS

In a previous study ferromanganiferous concretions had been found to occur generally in podsolic soils, not only in the acid but also in the alkaline horizons. The present study was initiated in an attempt to explain the manner in which iron and manganese are able to migrate to the centers of aggregation under such a wide range of conditions.

Most soils except those of a very sandy nature can be considered as gel systems modified by the presence of air spaces. Natural soils are thus three-phase systems in which convection as well as diffusion of materials may occur. But the heterogeneous composition of soils makes them undesirable as experimental media, and therefore more simple gels relatively free of impurities were used. These were agar, gelatin, electrodialyzed bentonite, and silica gels.

Stability and Diffusion of Sols.—In the first portion of the experimental work, colloidal suspensions (sols) of $Fe(OH)_3$, MnO_2, humus, Putnam clay, and gold were placed on top of the prepared gels and observations were made on their stability and diffusion. Sols of $Fe(OH)_3$ flocculated on all the gels used. MnO_2 sols flocculated on

bentonite but were stable on agar. The rate of diffusion in agar was less than 1 mm. per month. Sols of gold and Putnam clay behaved as did that of MnO_2. Humus sols were stable on all media and diffused at a moderate rate, about 2 to 4 mm. per day.

In an attempt to increase the stability of $Fe(OH)_3$ sols, it was found that the addition of small quantities of humus sols caused sensitization rather than protection. However, larger proportions of humus exerted a protective action on the $Fe(OH)_3$ sol. When the ratio of organic matter to Fe_2O_3 by weight exceeded 1 to 1, the stability of the $Fe(OH)_3$ sol was increased several fold. Such protected $Fe(OH)_3$ sols were stable on agar and diffused about 5 mm. per month. On bentonite, however, they flocculated and no diffusion occurred.

In view of these findings it was concluded that diffusion of iron and manganese oxids in the sol form in soils must be of very minor importance because the average soil represents a much more concentrated gel system than the ones used in this study, and consequently diffusion should occur less readily. Furthermore, conditions favoring flocculation recur at rather frequent intervals in soils. On the other hand, convection of the more stable sols thru the pores and channels in the soil should be of common occurrence. Migration of iron and manganese in the sol form by convection, however, was not considered adequate to account for the occurrence of all concretions.

Diffusion of Soluble Iron.—Inorganic ferrous and ferric salts diffused readily in acid gels. In neutral media not only did less iron diffuse, but its movement was slower. That hydrolysis of the iron salts might have altered the pH of the gel media was indicated by the appearance of a precipitate of $Fe(OH)_3$ in all the experiments. Hence it was impossible to define the relation between diffusion and the pH of the medium. Iron held in the anion of organic compounds, such as tartaric acid, diffused both in acid and alkaline media without any evidence of hydrolysis or precipitation.

When finely ground minerals containing iron were used as a source of ferrous ions, diffusion in acid bentonite occurred at nearly the same rate as previously observed with ferrous salts. When the pH of the bentonite gels was adjusted to various levels between 3.0 and 11.0, diffusion was observed in all, tho the rate was slower at the higher pH levels. Since powdered minerals tend to raise the pH of the media, it was certain that pH values were not lowered in the experiments.

In agar no diffusion of ferrous ions from mineral powders was detected. The diffusion of ferric ions from mineral powders could not be demonstrated with the methods employed.

Migration of Iron by Surface Diffusion.—To account for the diffusion of Fe^2 thru the bentonite systems its movement on the surface of the colloidal particles was postulated. Such an explanation seemed imperative because qualitative tests of the bentonite systems containing mineral powders showed the common diffusible anions to be absent; Fe^2 could not be detected in the ultrafiltrate; and solubility calculations predicted about .1 ppm. of Fe^2 in solution above pH 8.5. The hypothesis of surface diffusion was further supported by the following considerations:

1. Bentonite gels consist of two continuous phases, liquid and solid.

2. Adsorbed ions are held in a position that favors a surface movement.

3. The Gouy theory of the double layer predicts a low anion concentration at the bentonite surface, thus permitting a high ferrous ion concentration here regardless of the pH of the external medium.

4. Diffusion was more rapid in the more concentrated bentonite gel, a result contrary to that expected in liquid-phase diffusion.

5. Atoms and molecules have been reported to exhibit two-dimensional diffusion on several types of surfaces.

An hypothesis of surface diffusion of ferrous ions will account for the movement of iron to centers of concretion formation in soils containing excess $CaCO_3$. No other mechanism adequate to explain the translocation under these conditions is known.

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